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ORIGINAL RESEARCH

α′ Type Ti–Nb–Zr alloys with ultra-low Young's modulus and high strength

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Abstract α′ phase based Ti–Nb–Zr alloys with low Young's modulus and high strength were prepared, and their microstructure and mechanical properties were characterized. It was revealed that the lattice expansion by Nb and Zr addition as well as the presence of a few of α″ martensite might be responsible for the low modulus achieved. Ti–15Nb–9Zr alloy, with ultralow modulus of 39 GPa and high strength of 850 MPa, could be a potential candidate for biomedical applications.

1. Introduction

As typical materials for implant applications, commercially pure Ti (C.P. Ti) and Ti–6Al–4V alloy have been widely used as biomedical materials because of good biocompatibility, high specific strength, excellent corrosion resistance and lower elastic moduli compared with stainless steels and Co–Cr–Mo alloys [1,2]. Nevertheless, several concerns, e.g., the toxicity of elements like V, Al, and the so-called "stress shielding" caused by the modulus mismatch between the implants (∼110 GPa) and surrounding bone tissues (10–30 GPa) still exist in conventionally used titanium based biomaterials [3–5].

Because of the intrinsically lower modulus compared to α- and α+β based titanium alloys, a series of β-type titanium alloys as candidates for biomedical applications have been developed recently by adding nontoxic elements as β stabilizers or strengthening alloying elements, including Nb, Mo, Ta, Zr and Sn [6–10]. According to the physical metallurgy of titanium alloys, large amount of β stabilizing elements have to be incorporated to retain the β phase at room temperature by quenching. Actually, most of the recently developed biomedical titanium alloys with low Young's modulus contain considerable amount of Nb or/and Ta for stabilizing β phase [11–13]. These alloys hence possess much higher cost than pure titanium and Ti–6Al–4V owing to the addition of expensive Nb and Ta. In addition, large amount of heavy elements such as Nb, Ta, Mo and Sn inevitably lead to a considerable increase of the density of the β-type titanium alloys. Therefore, research and development of biomedical titanium alloys with low cost, low Young's modulus and light weight

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are of technical importance to broaden the applications of biomedical titanium alloys.

As is well known, some β stabilizing elements, such as Nb, Ta, Mo and Zr, could be completely miscible with Ti in specific β phases. By contrast, α phase in titanium alloys could dissolves much lower content of β stabilizers, and performs higher elastic modulus, exceeding 110 GPa in pure titanium or titanium alloys containing a few of β or α stabilizing elements. It has been recognized that α′ phase, a metastable phase formed martensitically by quenching, exhibits the same crystal structure with α phase. However, the metastable α′ phase could dissolve higher content of β stabilizers than stable α, and performs a decline in modulus with increasing β stabilizers [14,15]. Early studies attribute the decline in modulus to the co-existence of retained metastable β phase which transforms to stress-induced martensite on loading and then results in the lowering of elastic modulus [16]. Recent experimental results suggested that low Young's modulus could be achieved in 100% martensitic Ti–Mo (72 GPa) and Ti–Ta (65 GPa) alloys without retained metastable β phase [15,16]. The decreasing modulus seems to be associated with the β stabilizing elements which disturb and reduce the bonding force of the lattice by expanding unit-cell volume [17,18]. According to this proposition, there is a possibility to fabricate α′ based biomedical titanium alloys with low modulus and high strength by incorporating proper nontoxic β stabilizing elements and controlling the microstructures.

As typical nontoxic elements, Nb and Zr have outstanding large atomic radii and possess high solubility in titanium alloys. In the present study, Nb and Zr were selected as alloying elements to develop α′ based biomedical titanium alloys with low Young's modulus. The microstructural revolution and mechanical behavior of Ti–Nb–Zr alloys were characterized.

2. Experimental

Ternary alloys Ti–(5,10,15)Nb–9Zr (in wt%) were prepared by arc melting in an argon atmosphere using high-purity Ti, Nb, and Zr as raw materials. In order to isolate the effect of the addition of Zr (9%) on the lattice expansion, binary Ti–(5,10,15)Nb alloys were fabricated for comparison. The button ingots were homogenized at 1223 K (950 °C) for 5 h, followed by quenching into water at room temperature (298 K (25 °C)). The ingots after homogenization were cold rolled into plate of 1.0 mm in thickness, at a reduction of 85%. Parts of the cold-rolled specimens were solution treated at 1173 K (900 °C) for 1 h followed by quenching into water at room temperature. Phase constitutions of the specimens were characterized by X-ray diffraction (XRD) using CuK_α radiation. Microstructures were observed on an optical microscope (OM) and a FEI Quanta 200F (FEI Corporation, Hillsboro, OR) transmission electron microscope (TEM) operating at a voltage of 100 kV. Uniaxial tensile tests were conducted on an Instron-8801 testing system at room temperature at a strain rate of $1\times10^{-4}\ s^{-1}$. The specimens for tensile test, with a gage length of 30 mm and a cross section of $1\times1.5\ mm^2$, were spark cut from as-rolled plates. During tensile tests, a strain extensometer was used to record elastic strain of the specimens and Young's modulus.

3. Results and discussion

Fig. 1 shows the XRD profiles of solution treated Ti–(5,10,15)Nb–9Zr specimens, indicating that the alloys containing 5Nb and 10Nb are composed of single α′ phase (hexagonal structured martensite). While in the microstructure of Ti–15Nb–9Zr specimen, a small amount of α″ phase (orthorhombic martensite) was identified in addition to predominant α′ martensite. The XRD characterization of the specimens subjected to severe cold rolling indicated that their phase constitutions are similar to those of solution treated specimens, though drastic cold deformation leads to broadening of diffraction peaks due to stress and grain refinement. This is compatible with the early experimental results derived in binary TiNb alloys, i.e. the critical composition range at which α′ and α″ coexist is adjacent to 10.5 wt% Nb [16]. This suggests that the addition of Zr, a neutral element in titanium alloys, does not considerably influence the formation of α′ and α″ phases in TiNbZr alloys. Nonetheless, it was found that with the increasing Nb addition all the diffraction peaks of α′ phase moves towards low angle direction, suggesting a dilation of the lattice by the addition of Nb. By calculating the spacing of the crystal planes, typical (002) basal plane and (100) prismatic plane of close-packed hexagonal α′ phase for different specimens, the corresponding lattice parameters *c* and *a* were determined. The calculation revealed that the addition of Nb and Zr result in remarkable dilation of the unit-cell volume by expanding the lattice parameters, i.e. *c* and *a*. With comparison to the unit-cell volume of $0.106\ nm^3$ for pure α titanium ($c=0.468$ nm and $a=0.295$ nm), the unit-cell volume of Ti–(5,10,15)Nb–9Zr alloys are increased to $0.108\ nm^3$, $0.10\ nm^3$ and $0.110\ nm^3$, respectively. In order to assess the effect of the addition of Zr (9%) on the lattice expansion binary Ti–(5,10,15)Nb alloys were prepared in the present study. XRD characterization indicated that the unit-cell volume of Ti–(5,10,15)Nb alloys are, respectively, $0.107\ nm^3$, $0.107\ nm^3$ and $0.108\ nm^3$, convincing the significant role of both Nb and Zr played in the lattice expansion of Ti–Nb–Zr alloys.

Fig. 2 shows the OM image and the TEM micrograph together with selected-area diffraction (SAD) pattern taken from the martensite plate in solution treated Ti–15Nb–9Zr specimen. The OM image reveals that the acicular martensites with different orientations are distributed in coarse grains in the size of several hundred micrometers. Referring to the TEM image and the corresponding SAD pattern, the acicular plates are α′ martensites

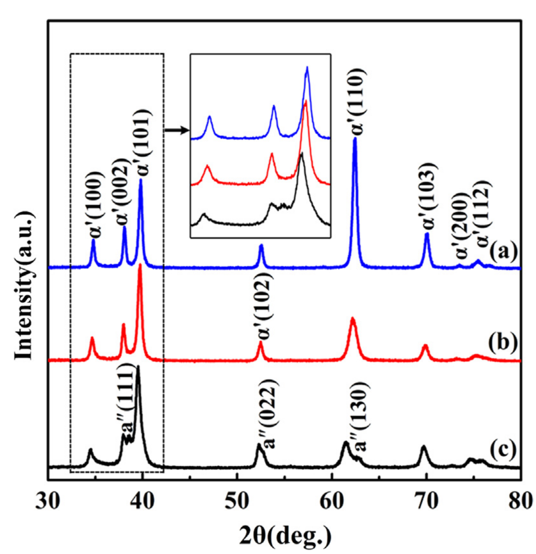

Fig. 1 XRD profiles of solution treated specimens: (a) Ti–5Nb–9Zr, (b) Ti–10Nb–9Zr and (c) Ti–15Nb–9Zr.

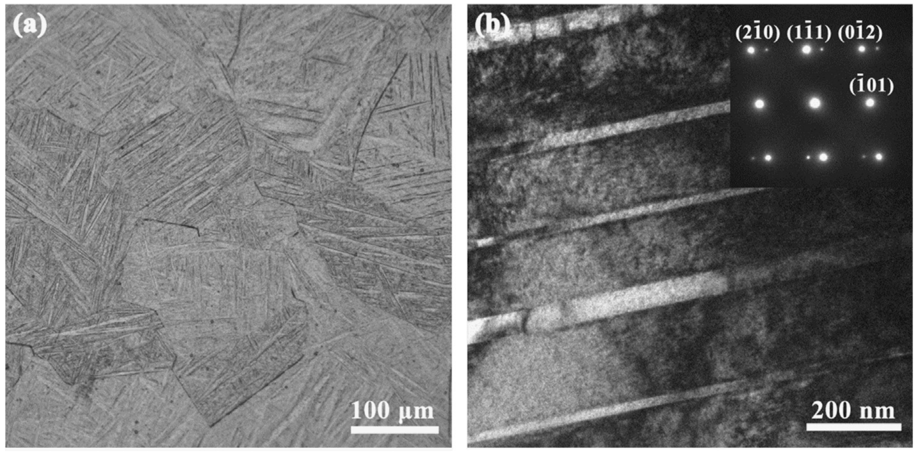

Fig. 2 (a) OM image and (b) TEM micrograph together with SAD pattern of solution treated Ti–15Nb–9Zr. The SAD pattern is taken from the martensite plate at the beam direction [0 1 $\bar{1}$ 1]α′.

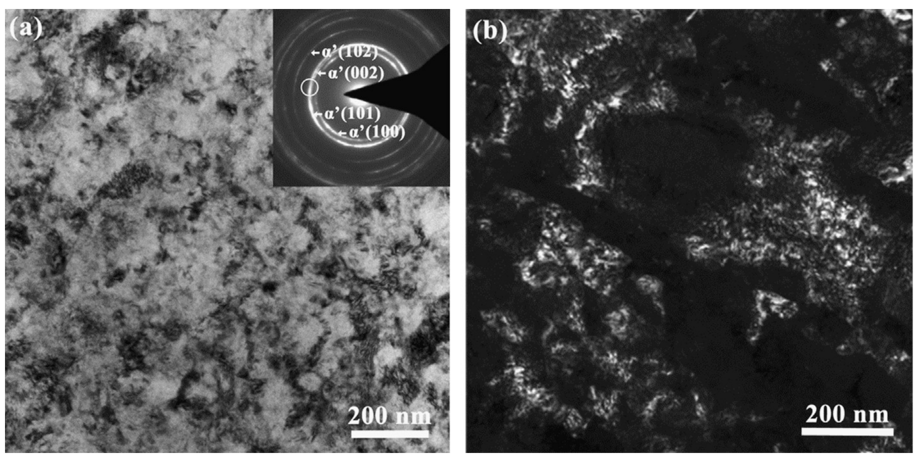

Fig. 3 TEM images of cold rolled Ti–15Nb–9Zr: (a) bright field image and the corresponding SAD pattern and (b) dark field image by the reflection indicated by the white circle in SAD pattern.

in close-packed hexagonal crystal structure and have classical internal twins structure.

Fig. 3 shows the bright field and the corresponding dark field TEM micrographs of Ti–15Nb–9Zr after severe cold rolling. It was found that after the cold rolling treatment, acicular shaped martensite plates observed in solution treated specimen disappear and the corresponding microstructure are composed of fine grains together with a lot of dislocation tangles. The SAD pattern exhibits near continuously dotted rings, as in Fig. 3a, verifying the refinement of martensite grains by severe cold deformation.

Young's moduli of solution treated and cold rolled Ti–(5,10,15) Nb–9Zr alloys were examined by tensile tests, and the corresponding stress–strain curves are shown in Fig. 4 in which Young's moduli values are listed. It is clearly seen that after cold rolling treatment all the alloys were remarkably strengthened with comparison to their solution treated counterparts. Undoubtedly, this significant strengthening is closely associated with the refinement of grains and generation of large amount of dislocations during cold rolling deformation. Note that Young's moduli are closely dependent on the Nb addition, i.e. higher content of Nb leads to lower Young's modulus. Particularly, Ti–15Nb–9Zr performs much lower modulus than the alloys with 5% Nb and 10% Nb, irrespective of the solution treated or cold rolled specimens. Though the cold rolling treatment gave rise to a decrease in Young's moduli of 5% Nb and 10% Nb alloys, the modulus of Ti–15Nb–9Zr was almost unchanged before and after the cold rolling process, i.e. 39 GPa for solution treated specimen and 38.8 GPa after cold rolling.

By comparing the dependence of Young's modulus on the Nb addition in Ti–(5,10,15)Nb–9Zr alloys, it is interesting to find that the increasing Nb from 5% to 10% leads to soft decline in modulus, for example, from 72.4 GPa to 67.2 GPa for solution treated specimens, and from 62.3 GPa to 54.4 GPa for cold rolled specimens. However, with further increase of Nb from 10% to 15%, a sharp decline in modulus occurred in both solutions treated and cold rolled Ti–15Nb–9Zr. Thus, ultralow Young's modulus of 39 GPa compatible with high strength of 850 MPa was achieved in cold rolled Ti–15Nb–9Zr alloy.

Regarding to low Young's modulus of α′ phase based titanium alloys, early researchers claimed the decline in modulus of α′ based binary titanium alloys to retained metastable β phase which transforms to stress-induced martensite during loading [16]. Later experimental results suggested that the addition of β stabilizers could reduce the bonding force of the lattice by expanding unit-cell volume, realizing low modulus in full martensitic Ti–Mo (72 GPa) and Ti–Ta (65 GPa) alloys [15]. According to the present study, the lattice expansion resulted from the addition of Nb

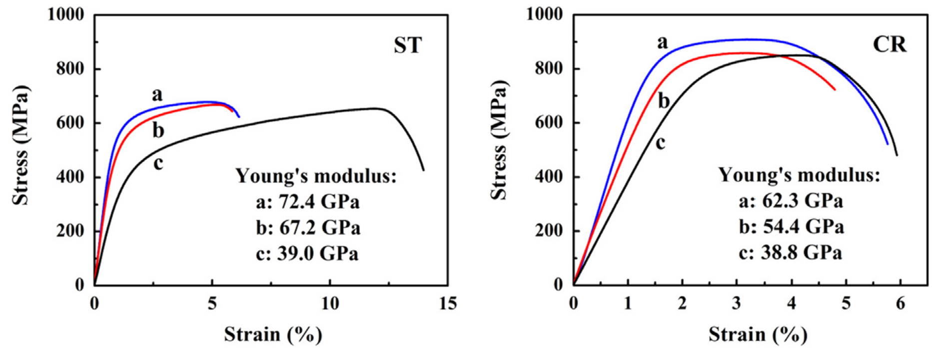

Fig. 4 Stress–strain curves of solution treated (ST) and cold rolled (CR) specimens: (a) Ti–5Nb–9Zr, (b) Ti–10Nb–9Zr and (c) Ti–15Nb–9Zr.

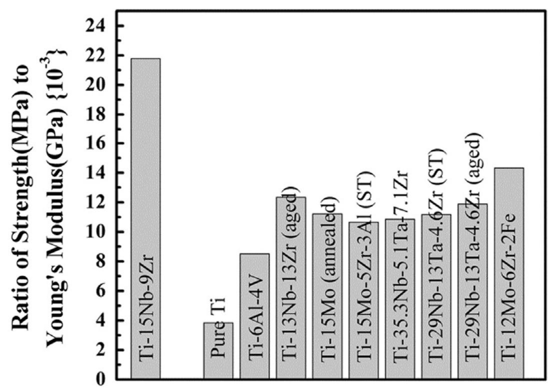

Fig. 5 The comparison of strength-to-modulus ratios of Ti–15Nb–9Zr alloy with some typical implant materials.

and Zr play an important role in deriving low Young's modulus. However, the experimental results of this study strongly suggested that the ultralow modulus might be closely associated with the presence of a few of α″ martensite. Although there is no retained β phase in Ti–Nb–Zr alloys for stress-induced transformation on loading, the presence of a few α″ phase could reduce modulus by reorientation of detwining of α″ martensite variants due to their thermoelasticity nature. This could be employed to explain the sharp decline in Young's modulus when increasing the addition of Nb from 10% to 15%, achieving ultralow modulus in α′ type Ti–15Nb–9Zr alloy.

As a key indicator, strength-to-modulus ratio is frequently employed to assess the performance of biomaterials requiring low modulus and high strength [13]. Fig. 5 shows the comparison of strength-to-modulus ratios of Ti–15Nb–9Zr alloy and typical implant materials. Ti–15Nb–9Zr possesses higher strength-to-modulus ratio than those of the typical implant materials, such as commercial pure Ti, Ti–6Al–4V and Ti–13Nb–13Zr, etc. It is reasonable to believe that the Ti–15Nb–9Zr alloy could be a potential candidate for biomedical application because of its outstanding strength-to-modulus ratio, low cost and light weight compared to conventional β type biomedical titanium alloys.

4. Conclusions

In summary, a preliminary experimental study was carried out to develop α′ phase based biomedical Ti–Nb–Zr alloys with low Young's modulus and high strength. Young's modulus as low as 39 GPa and ultimate strength of 850 MPa was achieved in Ti–15Nb–9Zr alloy. Both the lattice expansion by the addition of Nb and Zr as well as the presence of a few of α″ martensite were believed to be responsible for the ultralow modulus. With lower Young's modulus, lower cost and lighter weight compared to conventional β type biomedical titanium alloys, the Ti–15Nb–9Zr alloy could be a potential candidate for biomedical application.

Acknowledgments

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References

[1] M. Long, H.J. Rack, Biomaterials 19 (1998) 1621–1639.
[2] M. Geetha, A.K. Singh, R. Asokamani, A.K. Gogia, Prog. Mater. Sci. 54 (2009) 397–425.
[3] J.-Y. Rho, T.Y. Tsui, G.M. Pharr, Biomaterials 18 (1997) 1325–1330.
[4] M. Niinomi, Metall. Mater. Trans. A 33 (2002) 477–486.
[5] A. Biesiekierski, J. Wang, M. Abdel-Hady Gepreel, C. Wen, Acta Biomater. 8 (2012) 1661–1669.
[6] T. Saito, T. Furuta, J.-H. Hwang, S. Kuramoto, K. Nishino, N. Suzuki, R. Chen, A. Yamada, K. Ito, Y. Seno, T. Nonaka, H. Ikehata, N. Nagasako, C. Iwamoto, Y. Ikuhara, T. Sakuma, Science 300 (2003) 464–467.
[7] S. Guo, B. Chen, Q.K. Meng, R.W. Zhao, X.Q. Zhao, Prog. Nat. Sci.: Mater. Int. 23 (2013) 1–6.
[8] S. Guo, Q.K. Meng, G.Y. Liao, L. Hu, X.Q. Zhao, Prog. Nat. Sci.: Mater. Int. 23 (2013) 174–182.
[9] X. Zhao, M. Niinomi, M. Nakai, G. Miyamoto, T. Furuhara, Acta Biomater. 7 (2011) 3230–3236.
[10] S.J. Li, M.T. Jia, F. Prima, Y.L. Hao, R. Yang, Scr. Mater. 64 (2011) 1015–1018.
[11] T. Ahmed, M. Long, J. Silvestri, C. Ruiz, H.J. Rack, Titanium 1995 Science and Technology, The Institute of Metals, London1760–1767.
[12] D. Kuroda, M. Niinomi, M. Morinaga, Y. Kato, T. Yashiro, Mater. Sci. Eng.: A 243 (1998) 244–249.
[13] H. Matsumoto, S. Watanabe, S. Hanada, J. Alloy. Compd. 439 (2007) 146–155.
[14] H. Matsumoto, S. Watanabe, N. Masahashi, S. Hanada, Metall. Mater. Trans. A 37 (2006) 3239–3249.
[15] Y.L. Zhou, M. Niinomi, T. Akahori, Mater. Sci. Eng.: A 371 (2004) 283–290.
[16] G. Lütjering, J.C. Williams, Titanium, second ed. Springer-Verlag, Berlin18–31.
[17] Y. Song, D.S. Xu, R. Yang, D. Li, W.T. Wu, Z.X. Guo, Mater. Sci. Eng.: A 260 (1999) 269–274.
[18] H. Matsumoto, S. Watanabe, S. Hanada, Mater. Sci. Eng.: A 448 (2007) 39–48.